XXIX. — ON THE COMPOSITION OF A SOUTH AMERICAN PETROLEUM.

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Presented October 14, 1896.

It has long been known that large deposits of petroleum are to be found in various districts in South America, but beyond a limited use of the crude oil in lubrication, until recently no demand has been created for this petroleum. In the Argentine Republic are found heavy oils that deposit paraffine on distillation. In an examination of these oils by Engler and Ottin, hydrocarbons were found of the series C_nH_{2n+2} and C_nH_{2n}; they are said to yield a good illuminating oil. The oil fields of Peru and Bolivia have long been known, and large quantities of petroleum products are here obtained. The most promising oil fields hitherto in South America are those of Venezuela, and those deposits are receiving more attention in the preparation of commercial products.

The peculiar character of South American petroleum was brought to the attention of one of us (Mabery) in an examination which he was called upon to make by Mr. Horace M. Wilson of Cambridge, Mass., who collected a specimen of oil while prospecting along the Magdalena River in the United States of Colombia. A few miles from the river, in a rocky section of country, he discovered oil oozing up through a pool of water from a fissure in the rocks below. Oil was also observed escaping in bubbles through the water in a brook, where it formed a beautiful green layer three yards square. These sources and another within a range of two thousand feet were the only ones observed in a distance of fifteen miles. The geological formations in this section consisted of sandstones and shales tilted in nearly a horizontal position. At a distance of forty miles was a very large deposit of asphalt, hard and brittle like coal. About eighty gallons of this oil was collected at a rate of five gallons in twenty-four hours, of which the larger portion mixed with lard oil was used as a lubricator on car axles, for which it was found to be well adapted. Mr. Wilson brought home fifteen gallons of the oil, which was placed at our disposal for this examination.

The crude oil gave as its specific gravity 0.9480 at 20°. It is a high sulphur oil, as shown by the following determinations: (I.), 0.70; (II.), 0.66 per cent. It absorbed bromine equivalent to 12.09 per cent. It also contains a large quantity of nitrogen, as shown by the following determinations: (I.), 0.321; (II.), 0.315 per cent. A determination of ash in the crude oil was made, in which 29.1360 grams of the oil was burned, and the ash ignited until all carbon was consumed. The residue weighed 0.313 gram, equivalent to 0.011 per cent, or the same amount of ash as is obtained from Ohio crude oil.* The ash contains much iron, as shown by its brown color.

Determinations of carbon and hydrogen in the crude oil gave the following results: —

	I.	II.
C	85.80	85.45
H	12.02	11.79

The crude oil was dark in color, thick and viscous, flowing very slowly at ordinary temperatures. In attempting to distil it under ordinary atmospheric pressure, nothing came over below 260°, and between this point and 345° it distilled in the following proportions, beginning with 290 c.c.: —

	—310°	310°–345°
	70 c.c.	70 c.c.
Specific gravity,	0.8749	0.8615
Bromine absorption,	8.46	34.96

As the great increase in bromine absorption shows, the distillate 310°–345° was badly cracked, and it had the very disagreeable odor of the worst decomposition products of high petroleum distillates. The lower fraction had only the natural odor of an undecomposed distillate. Nothing could be distilled above 345°, and the residue was completely coked. In respect to the instability of its least volatile portions, this oil differs from any North American oil that has come under my observation (Mabery). It was therefore evident that another method of distillation must be resorted to with any hope of separating without decomposition the principal constituents.

In subjecting the crude oil to distillation *in vacuo* under 50 mm., the first distillate came over at 100°, and below 250° the following weights

* Proc. Amer. Acad., XXXI. 20.

were collected from 14.5 kilos, after the fourth distillation. It cannot be assumed that the absence of more volatile constituents was the result of evaporation by exposure on the surface of the water where the oil was found, since it was collected as soon as it appeared. No doubt such volatile portions as constitute gasoline on long exposure under such circumstances would be lost, but not constituents such as higher members of the series C_nH_{2n+2}, which do not appear in this oil.

	—130°	130°–135°	135°–140°	140°–150°	150°–155°	155°–160°	160°–165°
Grams	265	100	115	225	200	65	95
Sp. gr.					0.8706	0.8736	0.8747

	165°–170°	170°–175°	175°–180°	180°–185°	185°–190°	190°–195°
Grams	130	130	70	125	115	155
Sp. gr.	0.8784	0.8806	0.8846	0.8858	0.8867	0.8884

	195°–200°	200°–205°	205°–210°	210°–215°	215°–220°	220°–225°
Grams	140	165	95	110	100	145
Sp. gr.	0.8926	0.8947	0.8964	0.8989	0.9020	0.9045

	225°–230°	230°–235°	235°–240°	240°–245°	245°–250°	+250
Grams	145	150	100	93	75	130
Sp. gr.	0.9078	0.9113	0.9137			

Distillation of the fractions below 150° amounting to 700 grams was continued under atmospheric pressure, collecting within the limits of two degrees. After five distillations, ten in all from the beginning, heaps collected at 170°, 190°, and 212°, although in small quantities. The distillation could not be pushed too far on account of decomposition. The fraction 170°–172° (730 mm.) gave the following percentages of carbon and hydrogen: —

0.1456 grams of the oil gave 0.4556 gram CO_2, and 0.1864 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.71	85.33
H	14.29	14.23

Unfortunately there was not enough of this fraction to determine its specific gravity. A determination of sulphur gave 0.05 per cent. Its bromine absorption was found to be 3.5 per cent. No other heap appeared in the distillates below 190°. At 190°–192° more collected, evidently corresponding to a hydrocarbon boiling at 196°. A determination of the specific gravity of this distillate gave 0.8331. It absorbed bromine

amounting to 3.56 per cent. A determination of sulphur gave 0.10 per cent. A combustion gave the following percentages of carbon and hydrogen: —

I. 0.1696 gram of the oil gave 0.5332 gram CO_2. The water was lost.
II. 0.1542 gram of the oil gave 0.4846 gram CO_2, and 0.1912 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found. I.	Found. II.
C	85.71	85.73	85.69
H	14.29		13.78

This distillate was treated with a mixture of nitric and sulphuric acids, then with fuming sulphuric acid. In the first treatment, a very small quantity of a nitro compound separated as on oil, showing a trace of an aromatic hydrocarbon. The fuming acid produced no appreciable action.

A determination of carbon and hydrogen in this product gave the following results: —

0.1618 gram of the oil gave 0.5019 gram CO_2, and 0.2087 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	85.47
H	14.29	14.33

A determination of the specific gravity of the oil after this treatment gave 0.8333. Besides the very small proportion of aromatic hydrocarbon C_nH_{2n-6}, evidently this distillate is composed of a single body, although analysis alone is not sufficient to determine whether its composition is represented by the formula $C_{11}H_{22}$ or $C_{12}H_{24}$.

Above 192°, no distillates collected in appreciable amounts below 210°. At 212°–214° a larger quantity collected, evidently corresponding to a hydrocarbon boiling at 216°, which has been found in other oils. A determination of its specific gravity gave 0.8483. It absorbed bromine equivalent to 4.29 per cent, and contained 0.04 per cent of sulphur. A determination of carbon and hydrogen gave the following percentages: —

0.1555 gram of the oil gave 0.4887 gram CO_2, and 0.1992 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	85.71	85.72
H	14.29	14.23

A small quantity of nitro product was formed, when this distillate was treated with nitric and sulphuric acids, and fuming sulphuric acid then

removed more of the nitro compound from the oil. The oil shaken with sodic hydrate imparted a yellow color to the alkaline solution; it was then redistilled for analysis: —

0.1590 gram of the oil gave 0.4984 gram CO_2, and 0.2037 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	85.48
H	14.29	14.23

A determination of the specific gravity of the oil after treatment with acids gave 0.8484, the same value as was obtained for the crude distillate. It is therefore evident that this petroleum consists mainly of a single series of hydrocarbons, with a mere trace of aromatic hydrocarbons C_nH_{2n-6}. What this series is does not appear from these results, at least so far as its relation to the series of hydrocarbons hitherto discovered in petroleum. In the proportions of carbon and hydrogen, the series C_nH_{2n} is indicated. Neither the crude oil nor any of these distillates deposit paraffine, even at low temperatures. The higher distillates are thick and viscous, light yellow in color, and unquestionably are undecomposed constituents of the crude oil.

With nitric and sulphuric acids the constituents described in this paper are as slightly affected as are the naphtenes in the Russian oil. This fact, together with the results of analysis corresponding to the series C_nH_{2n-6}, and the high specific gravity, point to a similar composition for these bodies, and the small proportion of the crude oil distilling below 220° seems, therefore, to be composed almost exclusively of naphtenes, which is the first instance of an American petroleum having been found containing these hydrocarbons in any considerable quantity. The higher distillates from this petroleum will receive further attention in connection with the corresponding portions of other American oils.

Having at hand a specimen of petroleum from Oregon, resembling the heavier California products, with a specific gravity nearly the same as that of the South American oil described above, it seemed of sufficient interest to submit it to an examination in connection with that of the South American oil. The crude oil was very thick and dark, with a specific gravity, 0.9597 at 20°. Like the California oils, as shown by Peckham, it contains a large percentage of nitrogen compounds. A Kjeldahl determination gave 0.868 per cent of nitrogen. This is also a high sulphur oil, as shown by a combustion which gave 1.19 per cent of sulphur. It is also a high carbon oil; a combustion gave 86.06 per cent of carbon, and 11.87 per cent of hydrogen. A very small proportion

distils under atmospheric pressure without decomposition; even under diminished pressure, the amounts distilling below 250° are small.

In attempting to separate the constituents of this oil from the distillates first collected *in vacuo*, the portions below 250°, about the same in amount as the corresponding distillates from the South American oil, were carried through ten distillations under atmospheric pressure, which brought together larger quantities at 169°–170°, 190°–191°, and 212°–214°. The portions collected at 85°–150° in the first distillation gave as its specific gravity at 20°, 0.8755; the distillate 150°–225°, 0.9038; and the distillate 225°–250°, 0.9271. After the tenth distillation, the fraction 170°–171° gave as its specific gravity, 0.8200; the fraction 189°–190°, 0.8330; and the fraction 212°–214°, 0.853. A combustion of the fraction 189°–190° gave the following percentages of carbon and hydrogen: —

0.1510 gram of the oil gave 0.4757 gram CO_2, and 0.1835 gram H_2O.

C	85.90
H	13.51

After purification with nitric and sulphuric acids, the composition of this oil was not essentially changed: —

0.1484 gram of the oil gave 0.4643 gram CO_2, and 0.1839 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.33
H	14.29	13.77

The fraction 212°–214°, without purification, gave the following results: —

0.1457 gram of the oil gave 0.4625 gram CO_2, and 0.1757 gram H_2O.

C	86.46
H	13.40

By treatment with a mixture of nitric and sulphuric acids, and then with fuming sulphuric acid, this distillate was only slightly affected: —

0.1343 gram of the oil gave 0.4231 gram CO_2, and 0.1677 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.90
H	14.29	13.88

Unfortunately the quantities of these distillates were too limited to permit of further examination. The principal object, however, — to ascer-

tain whether any members of the series C_nH_{2n+2} were present at all, or the aromatic hydrocarbons C_nH_{2n-6} in more than minute proportions, — was attained. Evidently the main body of this oil is composed of a series with less hydrogen than the former and more than the latter. The oil distills in such small quantities, even *in vacuo,* below 220°, it will be interesting to ascertain the composition of the distillates above this point.